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Review

Sterically induced differences in N-heterocyclic carbene transition metal complexes

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ABSTRACT

The steric implications of the wingtip groups and tether length in bidentate N-heterocyclic carbene ligands on the structural features of NHC complexes are still not fully understood. Steric crowding causes pitch and yaw angles of unsymmetrically coordinated NHC ligands, equatorial or axial coordination of the carbene in trigonal bipyramidal complexes and the close approach of halogen atoms to the C2 atom in some complexes, although electronic factors have been implicated in all instances.

1. Introduction

N-heterocyclic carbenes, NHC, popular ligands ever since their first isolation some twenty years ago, sparked not only a renaissance [1–3] of their transition metal chemistry, but prompted the development of a host of related stable carbenes of unprecedented and rich diversity [4]. As these carbenes "traditionally" replace the ubiquitous phosphane ligands in transition metal complexes [5], questions relating to their stereoelectronic properties are increasingly important for the rational design of NHC ligands [6], especially for applications in catalysis. The modification of wingtip[1] substituents and alterations of the imidazole ring have notable influences on their electronic properties due to annelation [7,8] and their steric properties due to folding [9]. The early perception that NHC act solely as innocent spectator ligands had to be revised in view of the observed reductive elimination of imidazolium salts from transition metal alkyl complexes with *cis*-NHC ligands, a main catalyst degradation pathway [10,11] (see Fig. 1).

The main contribution to the stability of NHC or Wanzlick–Arduengo carbenes comes from a combination of the large electron withdrawing effect of the electronegative nitrogen atom on the σ-electrons of the C–N single bond paired with a $\pi_N \rightarrow \pi_C$ back-donation via the p-orbitals [12–14]. The presence of a C=C double bond in the backbone provides additional thermodynamic stabilisation of at least 20 kcal/mol [15]. To destabilise the $N_{p\pi} \rightarrow C_{p\pi}$ interaction and make the "empty" p-orbital on carbon available for a donor interaction, π-electron density has to be withdrawn from the nitrogen p-orbital, either by annelation [7,8,16] or by introducing

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[1] Wingtip or wingtip group is an established term and denotes the N-substituents on the NHC. The term arises from the likening of the Wanzlick–Arduengo carbene's structure to a bird in flight with the N-substituents as the wings.

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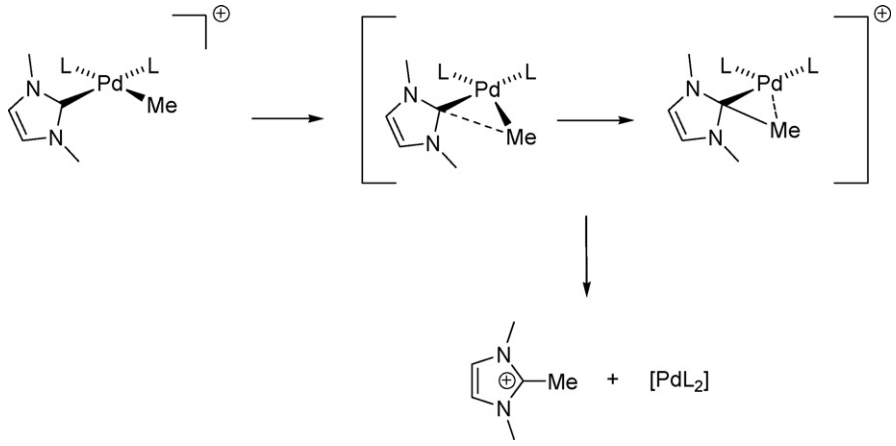

Fig. 1. Reductive elimination of 2-alkylimidazolium salts from transition metal NHC complexes.

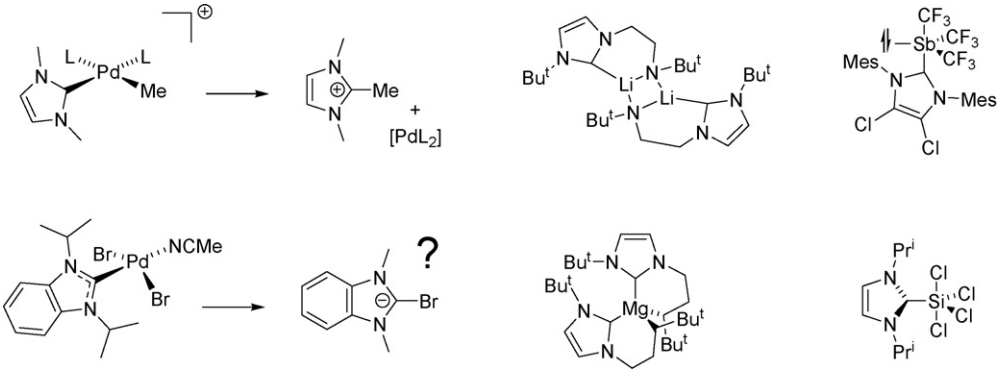

Fig. 2. Three pairs of structurally different NHC complexes.

suitable electron withdrawing substituents on the imidazole backbone (C4/C5) [8]. There is strong experimental evidence against the possibility of a Wanzlick–Arduengo carbene to act as a Lewis acid or electrophile towards a σ-donor ligand [17]. There is only limited π-backbonding observed in transition metal NHC complexes precisely because the receiving p-orbital on carbon is already sufficiently filled with π-electron density from the nitrogen lone pairs. The π-acceptor strength of NHC is believed to be rather low [18], although it is no longer thought to be negligible [19]. It is well known that despite the excellent σ-donicity of NHC, excess of free NHC added to transition metal NHC complexes does not result in a bonding interaction between the lone pair of the singlet carbene and the p-orbital of the coordinated NHC. No such interactions have been observed in crystal structures of free NHC, although electronically destabilised NHC are known to coexist with their dimers [20–22].

Against this background, could crystal structures that feature nucleophilic coligands in close proximity to the C2 p-orbital [23–25] be explained by steric considerations rather than by weak donor interactions into an already occupied orbital that is fully embedded into a delocalised 6 π-electron system? Could the unsymmetrical coordination of a tethered and chelating NHC ligand [26] not be explained by an insufficient tether length rather than undirected "ionic" bonding [27,28] and could the equatorial coordination of NHC ligands in a trigonal bipyramidal coordination geometry [24,29–31] not be caused by the steric demand of the wingtip groups rather than any irregularities of the NHC's electronic structure (see Fig. 2)? In its accustomed axial position [32,33], the wingtip groups of the NHC cannot avoid all three ligands in the equatorial plane simultaneously making steric clashes between the wingtip groups and third row elements in the equatorial plane inevitable.

The steric demand of an NHC ligand is largely governed by the planar imidazole ring creating a wedge like ligand whose steric properties can be described in terms of two angles – a small one describing the height of the wedge and a large one for its width – very similar to the phosphinidine ligands [34]. Alternatively, one can describe the steric demand of an NHC ligand in terms of the area it shades in the metal's coordination sphere, a parameter known as V_{burr} [6]. In either model, the wingtip substituents on the nitrogen atoms are easily identified as the determining factors for the steric demand of these carbene ligands.

The steric influence of the wingtip substituents on the structure of a transition metal carbene complex is most readily seen in the non-parallel coordination of the carbene ligands in the homoleptic [M(NHC)$_2$] complexes (M = Ni, Pd, Pt) [35–43] (see Fig. 3). The same structural features are observed in the cationic homoleptic group 11 complexes [M(NHC)$_2$]X (X = anion) [44–47]. It is perhaps inter-

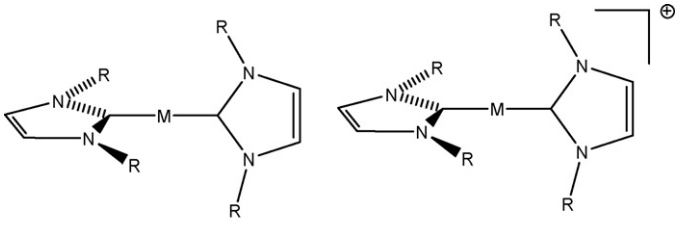

Fig. 3. Homoleptic and cationic *trans*-[M(NHC)$_2$] complexes.